

# METHOD FOR PRODUCING INORGANIC SEMICONDUCTOR NANOCRYSTALLINE RODS AND THEIR USE

## FIELD OF THE INVENTION

This invention relates to a method for synthesizing rod-shaped semiconductor nanocrystals, inter alia rod shaped Group III–V semiconductor nanocrystals.

## LIST OF REFERENCES

The following references are considered to be pertinent for the purpose of understanding the background of the present invention:

1. R. L. Wells et al., *Chem. Mater.* 1, 4 (1989).
2. A. P. Alivisatos and M. A. Olshavsky, U.S. Pat. No. 5,505,928.
3. A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng, A. P. Alivisatos, *Appl. Phys. Lett.* 69, 1432 (1996).
4. R. S. Wagner, in *Whisker Technology*, A. P. Levitt, Ed. (Wiley-Interscience, New York, 1970), pp.47–119.
5. A. M. Morales, and C. M. Lieber, *Science* 279, 208 (1998).
6. X. F. Duan, and C. M. Lieber, *Adv. Mater.* 12, 298 (2000).
7. Y. Cui, X. F. Duan, J. T. Hu, C. M. Lieber, *J. Phys. Chem. B* 104, 5213 (2000).
8. M. S. Gudiksen, L. J. Lauhon, J. F. Wang, D. C. Smith, C. M. Lieber, *Nature* 415, 617 (2002).
9. Gudiksen, J. F. Wang, C. M. Lieber, *J. Phys. Chem. B* 105, 4062 (2001).
10. J. F. Wang, M. S. Gudiksen, X. F. Duan, Y. Cui, C. M. Lieber, *Science* 293, 1455 (2001).
11. Y. Huang, X. F. Duan, Y. Cui, L. J. Lauhon, K. H. Jim, C. M. Lieber, *Science* 294, 1313 (2001).
12. J. D. Holmes, K. P. Johnston, R. C. Doty, B. A. Korgel, *Science* 287, 1471 (2000).
13. J. T. Hu, L. S. Li, W. D. Yang, L. Manna, L. W. Wang, A. P. Alivisatos, *Science* 292, 2060 (2001).
14. M. Kazes, D. Lewis, Y. Ebenstein, T. Mokari, U. Banin, *Adv. Mater.* 14, 317 (2002).
15. Y. Huang, X. F. Duan, Q. Q. Wei, C. M. Lieber, *Science* 291, 630 (2001).
16. X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* 404, 59 (2000).
17. A. P. Alivisatos et al., U.S. Pat. No. 6,225,198.
18. A. P. Alivisatos et al., U.S. Pat. No. 6,306,736.
19. U. Banin and Y. W. Cao, PCT Application WO 02/25745.
20. Y. W. Cao, and U. Banin, *J. Am. Chem. Soc.* 122, 9692 (2000).
21. T. J. Trentler, S. C. Geol, K. M. Hickman, A. M. Viano, M. Y. Chiang, A. M. Beatty, P. C. Gibbons, W. E. Buhro, *J. Am. Chem. Soc.* 119, 2172 (1997).
22. M. Brust et al., *J. Chem. Soc. Chem. Commun.* 801 (1994).

## BACKGROUND OF THE INVENTION

Miniaturization of electronic and optical devices requires semiconductors of nanometer size domain. Inorganic semiconductors, in particular Group III–V semiconductors, exhibit features that make them attractive for use in solid state electronics as well as optical devices (e.g., high thermal stability, high electron mobility, low energy band gap, and direct-band gap behavior).

Developing preparation methods of semiconductor nanocrystals has been an important branch of synthetic chemistry. For many of the semiconductors, syntheses

through the reaction of simple reactants have been proved to be impossible, thus only until recent years, some of them can be prepared through the use of organometallic precursors in organic solvents. The typical examples are Group III–V semiconductor nanocrystals, which are formed by dissolving a Group IIIa precursor and a Group Va precursor in a solvent and then applying heat to the obtained mixture of solvent and precursors. More specifically, Group III–V semiconductor nanocrystals may be produced by using silyl cleavage. Specifically, Group III halides have been reacted with  $E(\text{SiMe}_3)_3$ , where  $E=\text{P,As}$ , in hydrocarbon solvents to yield nanocrystalline III–V semiconductors [1].

Alivisatos et al. [2] described a process for forming Group III–V semiconductor nanocrystals wherein size control is achieved through the use of a crystallite growth terminator such as nitrogen- or phosphorus-containing polar organic solvent, for example pyridine, quinoline or mono-, di-, and tri-( $\text{C}_{1-6}$  alkyl)phosphines.

High quality group III–V semiconductor nanocrystals were produced by a method consisting of injecting the precursors into a hot coordinating solvent such as trioctylphosphine (TOP) [3].

All the above-mentioned processes can yield only spherically shaped nanocrystal semiconductors (also termed quantum dots) of the group III–V.

In the nanometer size domain the properties of semiconductors depend not only on size but also on shape. The growth of crystalline wire-like structures based on the vapor-liquid-solid (VLS) mechanism has been developed [4]. In the VLS method, a liquid metal cluster acts as a catalyst where the gas-phase reactants adsorb, subsequently leading to whisker growth from the supersaturated drop. Laser ablation was combined to form nanometer-sized metal clusters as catalysts with the VLS mechanism, to grow a variety of semiconductor nanowires, doped nanowires, and nanowire superlattices with lengths in the micrometer range [5–8]. The diameters of the nanowires could be tuned by changing the size of the catalyst clusters [9] and for silicon nanowires, the smallest diameter reported was 6 nm. For InAs and other III–V semiconductor nanowires, the average diameters are larger than 10 nm. Such diameters are at the onset of the strong quantum confinement regime providing rather limited band gap tunability by size effects. A whole set of optoelectronic devices including transistors, detectors and a light emitting diode were demonstrated using these nanowire building blocks [10, 11]. Micron long silicon nanowires with diameters of 4–5 nm were also prepared in a pressurized solution system by using gold nanocrystals as catalyst [12].

Rod-shaped nanocrystals are interesting because the rod shape produces polarized light emission leading to polarized lasing [13, 14]. Additionally, rod-shaped particles are suitable for integration into nano-electrode structures for the production of electronic devices such as sensors, transistors, detectors, and light-emitting diodes [11, 15]. A recent example of rod-shaped nanocrystals was described in relation with CdSe nanocrystals [16, 17]. Shape control in this case was realized by kinetically controlled growth along the special c-axis of wurtzite CdSe nanocrystals through the use of a mixture of surfactants. Such a process is not applicable for the growth of cubic-structured semiconductor nanorods, e.g. nanorods of a few important III–V semiconductors. Therefore a novel and completely different rod growth mechanism is needed for these compounds.

A process for the formation of shaped Group III–V semiconductor nanocrystals is described in U.S. Pat. No.